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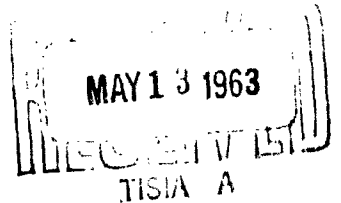
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A STUDY OF ION-ION AND ION-SOLVENT INTERACTIONS

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Annual Technical Report
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submitted by

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Section (a) - Abstract

The ultraviolet absorption properties of solutions of iodide ion in polar solvents has been discussed by Smith and Symons[s] in terms of a square-well model which crudely resembles the model adopted for the description of F-centres in alkali halide crystals. In the investigation reported below, the behaviour of bromide and chloride ions in similar solvents is discussed. It is shown that the ultraviolet absorption properties of bromide ion in water and methyl cyanide and chloride ion in methyl cyanide bear a striking resemblance to the behaviour of iodide ion in these systems. In addition, the tail of the absorption band of bromide ion in other polar solvents, e.g. alcohols, ethyl cyanide etc., also exhibits a similar parallelism in behaviour with the iodide ion and this conclusion is confirmed by observations of the behaviour of the absorption spectra in mixed solvent systems. The similarity in the temperature dependence of the position of the first absorption band for iodide, bromide and chloride in methyl cyanide is noted although the contributing factors which are responsible for this apparent independence of the size of the central ion remain a matter for speculation.

The concept of ion association is also recalled and the definitions, which are employed in this report, are explained. In this system two classes of ion pairs, i.e. contact and solvent-shared are spectroscopically significant. Solutions of tetra-n-butylammonium bromide in carbon tetrachloride exhibit an absorption band at 38,650 cm^{-1} which possesses similar properties to those of

tetra-n-butylammonium iodide in the same solvent. The band at
38,650 cm^{-1} is therefore attributed to that of a contact ion pair.
The effects of added methanol and added methyl cyanide on this band
are compared and it is shown that in both cases the contact ion pair
is progressively destroyed with the addition of the more polar
solvent but that methanol is more effective than methyl cyanide.

The presence of solvent-shared ion pairs is suggested to
account for the properties of the absorption bands exhibited by
solutions of iodide and bromide in methylene dichloride. An
investigation into the properties of the tail of the absorption
band exhibited by solutions of tetra-n-butylammonium bromide in
dioxan suggests that the electrolyte is also present in this form.

The effect of added methanol on the 34,480 cm^{-1} band exhibited
by solutions of tetra-n-butylammonium iodide has also been the
subject of a rigorous investigation. The absorption spectra
indicate that the stability of the contact ion pair is unaffected
by methanol concentrations up to $1 \cdot 6 \times 10^{-3}$ molal but that further
addition of methanol results in the destruction of the ion pair.
The mechanism of the destruction is shown by the absorption spectra
to proceed via the solvent shared ion pair to an essentially "free"
iodide ion. The data demonstrate the extreme efficiency of
methanol in destroying these ion pairs and it must be concluded
that, above a methanol concentration of 2×10^{-1} molal, the fraction
of electrolyte present as contact ion pairs is vanishingly small.
This conclusion is at variance with the conclusion arrived at after
an analysis of the conductivity of these systems and the definitions

employed here are briefly examined.

Section (b) - Main Body of the Report.

(1) Theoretical Background.

The characteristics of the ultraviolet absorption spectra exhibited by halide ions in both solutions and crystals has attracted a great deal of attention since the analysis of these spectra has been shown to reveal a better understanding of the effect of changes in temperature and environment on the properties of the halide ion. Platzmann and Franck[1] postulated that the electron in the excited state is not specifically bound by any one solvent molecule but exists in a '2s' type orbital which extends into the bulk solvent. Stein and Treinin[2], after an investigation into the effect of temperature on the first absorption band of the iodide ion in water, modified this approach although the electron is still considered to move out into the bulk solvent. An alternative approach, similar to that employed to describe F-centres in alkali halide crystals, was proposed by Smith and Symons[3] who considered that the electron in the excited state was confined within a 'square-well' which is defined by the oriented solvent molecules comprising the primary solvation layer. The effect of changes in environment and temperature on the position of the first absorption band is discussed, for any one halide ion, in terms of changes in the size or radius of the square-well. The energy corresponding to the frequency of maximum absorption of the first band, E_{max}, is related to the radius of the square-well, r_0, and the ionisation potential of the halide ion, I.P., by:-

$$E_{max} = I.P. + h^2/8mr_0^2 \qquad \text{---- (1)}$$

where h represents Planck's constant and m is the mass of the electron.[3]

On the basis of the square-well treatment, Smith and Symons predicted that a plot of E_{max} at a given temperature (usually 20°C) against the variation of E_{max} with temperature, dE_{max}/dT, for polar solvents will be a straight line with slope -T. Griffiths and Symons[4] have shown that the square-well treatment is in good agreement with the behaviour of iodide ion in many solvents, e.g. water, acetone, ammonia, methyl alcohol etc. The 'square-well' treatment is however not confined to the iodide ion and in the investigation undertaken during the tenure of the contract an attempt has been made to determine the effects of changes in temperature on the first absorption band of bromide and chloride ions in some of the solvents mentioned above.

(2) <u>Absorption Spectra of Bromide and Chloride Ions in some Polar Solvents.</u>

A complete investigation, similar to that reported for iodide ion,[4] is hindered by the increase in ionisation potential of these two ions[5,6] which results in a shift of the absorption bands to higher energies, in many cases, into the solvent absorption. In addition, the doublet splitting between the $^2P_{3/2}$ and $^2P_{1/2}$ ground states of the bromine atom,[7] 3,600 cm^{-1}, is smaller than that of the iodide ion, 7,170 cm^{-1}, with the result that the two absorption bands overlap to yield in many cases a single, broad absorption

band. The doublet splitting for the chlorine atom[8] is again
much smaller, 880 cm^{-1}, and only a single absorption band is
detected.

Materials

Solvents were dried and purified as described by Griffiths
and Symons.[9] Tetra-n-propylammonium and tetra-n-butylammonium
bromide were crystallised from mixtures of ethanol and acetone
and dried under vacuum, over phosphoric oxide, at room temperature.
Tetramethylammonium chloride was dried under vacuum over phosphorus
pentoxide at room temperature.

Apparatus

Ultraviolet absorption spectra were measured using Unicam
S.P.500 and Unicam S.P.700 spectrophotometers. The problems of
solvent absorption were minimised in most cases by using 0·1 mm
cylindrical stoppered silica cells.

Analysis of Spectra

The spectra of bromide ion in water shows a broad absorption
upon which is superimposed the oxygen absorption lines. Two
methods of analysis of this spectra were attempted. The first
method involved the submission of the experimental data to a
computer which has been instructed to give the best Gaussian shaped
absorption band.[10] Secondly, geometric analyses of the spectra[10]
which employed the method of rectilinear diameters and a value
for the doublet splitting also allowed an estimation of the position
of the first absorption band both in this and other solutions where
an absorption maximum was observed.

Results and Discussion

The values of E_{max}^{20}, dE_{max}/dT and extinction of the first absorption band for solutions of bromide and chloride ions in water and bromide in water are recorded in table 1 together with values obtained by other workers for comparison. In those solutions where the frequency corresponding to maximum absorption was not detected, the movement of the side of the absorption band at a fixed extinction coefficient, 2×10^3, was monitored. The results are summarised in table 2. An interesting system in this respect is the solution of bromide ion in 1:3 dioxalane for which an increase in temperature resulted in a shift in the absorption band with the result that an absorption maximum was detected at the higher temperatures. Another important characteristic of the absorption bands is their behaviour when another solvent is added. In mixtures of methyl cyanide and water, the band was found to move steadily between the positions of the abosorption bands in the pure solvents which resembles the behaviour observed in solutions of iodide ion. This behaviour was also observed for mixtures of methyl cyanide and the solvents listed in table 2.

Inspection of table 1 reveals that the values of dE_{max}/dT for the bromide ion are similar to those reported for the iodide ion[9]. Similarly the trend in values of the temperature dependence with frequency shown in table 2 resembles the trend observed for the behaviour of the absorption maximum of iodide ions in these solvents.

The marked similarity in the values of dE_{max}/dT for solutions of iodide, bromide and chloride ions in methyl cyanide is of

interest. On the basis of the square-well treatment, the temperature dependence of the absorption band is given by the expression:-

$$dE/dT = -(h^2/4\pi r_0^3)(dr_0/dT). \qquad\qquad --- (2)$$

It is unexpected therefore that on changing the central ion from iodide to bromide, to chloride, in methyl cyanide where the corresponding values of r_0, as determined by equation (1), are 4.47, 4.13 and 3.80Å respectively, that the value of dE_{max}/dT should remain constant. It appears that as the size of the ion decreases, there is an accompanying increase in the interaction between the ion and the solvent which tends to decrease the tendency of the ion cavity to expand with temperature.

However, the tentative conclusion is drawn that the square-well treatment is still reasonable for the treatment of the absorption spectra of all the halide ions in these solvents. It is recalled however that the Smith-Symons correlation diagram included the behaviour of iodide in alkali iodide crystals. It is intended to examine this aspect more fully with respect to the crystal data for all alkali halides.

(3) **Ultraviolet Absorption Spectra of Iodides and Bromides in Solvents which have a low dielectric constant.**

Introduction

In order to explain the properties of electrolytes in solvents of low dielectric constant, < 30, Bjerrum introduced the concept that a fraction of the dissolved electrolyte was present as ion pairs, the stability of which is controlled by coulombic forces only.

The precise definition of the term, ion pair, has been the subject of controversy since many methods and experimental techniques have been employed in the analysis of this phenomenon.[14,15] In order to resolve some of the resulting difficulties in nomenclature, and to explain the terms employed in those laboratories, Griffiths and Symons[9] have suggested the two spectroscopically significant classes of ion pairs outlined below.

(i) <u>Contact ion pairs</u> - Griffiths and Symons observed that the position of the absorption maximum exhibited by tetra-n-alkylammonium iodides in carbon tetrachloride was dependent on the nature of the cation but independent of temperature.[9] They concluded that the iodide ion was present in the form of a contact ion pair in which the electronic transition was from the iodide ion to a diffuse orbital defined by the cation.

(ii) <u>Solvent-Shared ion pairs</u> - The absorption band exhibited by solutions of tetra-n-butylammonium iodide in dioxan was attributed to the presence of solvent shared ion pairs. In an ion pair of this class, the two ions are separated by one solvent molecule which exists in the primary solvation shells of both ions. The nature of the observed transition for the iodide is discussed in terms of the square-well model although the cavity, within which the anion exists, is distorted by the close proximity of the cations. In these systems therefore the position of the absorption band will display a temperature dependence although the data will not fit the correlation diagram observed for halide ions in more polar solvents.

The results of an extention of the work reviewed above are presented in table 3 and in this section their significance is discussed.

The effect of temperature on the position of the first absorption bands exhibited by solutions of tetra-alkylammonium iodides in methylene dichloride indicated that while the value of $d\nu_{max}/dT$ was non-zero, it was smaller than the value predicted by the Smith-Symons correlation diagram. For solutions of bromide in dioxan, although the behaviour of the tail of the absorption was recorded, it can be seen, by comparison with the data presented in table 2, that the value of $d\nu/dT$ was also smaller than that expected on the basis of the position of the absorption band. It is suggested that in these three systems the salt was present in the form of solvent-shared ion pairs.

The position of the absorption band at 38,650 cm^{-1} exhibited by solutions of tetra-n-butylammonium bromide in carbon tetra-chloride was found to be independent of temperature. The effect of adding a small quantity of bromine to this solution resulted in the development of a new band at 36,000 cm^{-1} which indicates that this latter band is associated with the tribromide anion. The similarities between the behaviour of the iodide and bromide ions in carbon tetrachloride suggest that the species present is a contact ion pair. This conclusion is in agreement with the observations of the effect of added methyl cyanide on the 38,650 cm^{-1} band. The usual shift is not observed but there is a decrease in the intensity of the band accompanied by the production of a new band

at higher frequencies which resembles the band observed for bromide
ion in pure methyl cyanide. It is suggested that the solvent
mixtures contain both contact ion pairs and "free" bromide ions.

A similar phenomenon was also observed when methanol was added
to the solution in carbon tetrachloride although in this case the
effectiveness of the methanol in destroying the $38,650$ cm^{-1} band
was far greater than that of methyl cyanide. It is interesting
to note that the difference in the position of maximum absorption
of the bromide and iodide ion pair with constant cation, $4,170$ cm^{-1},
is almost double the difference in the ionisation potential of the
halide ions, $2,500$ cm^{-1}. It appears that a major contribution to
this discrepancy must arise from the difference in the radii of the
two ions which leads to an important change in the distance between
the centre of positive and negative charge within the ion pair.

The effect of added methanol on the absorption band exhibited
by tetra-n-hexylammonium iodide is a decrease in the intensity of
the band at $34,430$ cm^{-1}. Preliminary experiments indicated that
within a salt concentration range 2×10^{-6} to 13.5×10^{-6} the
extinction coefficient and position of the band was unaffected by
concentrations of methanol up to 1.6×10^{-8} molal. This observation
was unexpected since it was anticipated that with increase in salt
concentration, the concentration of methanol required to produce a
measurable decrease in intensity would also increase. Attention
was then directed to the effect of higher methanol concentrations
which were found to cause a decrease in extinction coefficient and
a shift of the band to higher energies. Isobestic points in the

36,000 cm^{-1} and 39,000 cm^{-1} regions were observed for methanol
concentrations between 1.6 x 10^{-8} and 4.8 x 10^{-8} molal. although
with further additions of methanol the isobestic points were not
observed and a steady decrease in the absorption over the whole
range, < 40,000 cm^{-1}, was observed.

These results suggest that the contact ion pair is slowly
destroyed, at methanol concentration greater than 1.6 x 10^{-8} molal,
through an equilibrium process.   Comparison with the behaviour of
iodide ion in other solvents such as methylene dichloride suggests
that the new species involved in the equilibrium may be a solvent-
shared ion pair.   This latter species is itself destroyed at higher
methanol concentrations and the absorption spectra suggest that
complete destruction of contact ion pairs is effected by methanol
concentrations of only 2 x 10^{-1} molal.   It is difficult however to
reconcile this conclusion with that arrived at after an analysis of
conductivity data,[16] which suggests that the contact ion pair is a
stable entity in carbon tetrachloride solutions which contain
methanol in far greater concentrations than those employed here.
Perhaps the methods involved in the analysis of conductivity data
are responsible for this dichotomy, since they are based on the
assumption that it is possible to extrapolate the equations
describing the behaviour of fully dissociated electrolytes in
highly polar solvents, to the behaviour of free ions in equilibrium
with ion pairs in solvents of low dielectric constant.   The
fraction of ions not present as free ions are predefined as contact
ion pairs.   Conversely however it appears possible that the

equations which are used to define the nature of the free ions also define the nature of the ion pairs and that the structure of the ion pairs so defined may vary with changes in the composition of the solvent. This is another example of how the nature of the experimental technique contribute towards the interpretation of the phenomenon of ion association.[16]

Implications for Future Work

In addition to the points noted in the text above, other problems have arisen as a natural corollary to our investigation. These include:-

(a) An examination of the contribution of the solvent and its molecular structure to the radius of the square-well cavity. The resolution of this problem may suggest the stereochemical arrangement of the solvent molecules contiguous to the ion.

(b) An examination of the behaviour of the halide ions in environments other than liquid phase.

(c) A continued examination of the structure of ion pairs in solution in order to understand the factors which control their stability.

(d) In the discussion of the ultraviolet absorption properties of halide ions in various solvent media, attention has been concentrated on the first absorption band. It is intended however to examine the nature of the absorption spectra at higher energies and to examine the nature of the transitions involved.

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Table 1 - Details of the first absorption band of bromide and chloride ions in water and methyl cyanide at 20°C

Solvent	Ion	$\bar{\nu}_{max}$ (cm^{-1})	$10^3 E_{max}$	dE_{max}/dT (cal/deg)	Ref.
Water	Br$^-$	50,960	12.3	42±8	
		51,000			11
		49,500 (22°C)			12
MeCN	Br$^-$	45,600	9.7	65±8	
		45,930			11
		46,080 (22°C)			12
	Cl$^-$	51,200			
		51,160			11
		50,760 (22°C)			12

Table 2 - Effect of temperature on the tail of the first absorption band of the bromide ion at a fixed extinction coefficient, 2×10^3, in various solvents at 20°C.

Solvent	$\bar{\nu}_{max}$ cm^{-1}	dE/dT cals.deg^{-1}
Ethanol	48,700	41
Methanol	48,700	41
n-butanol	48,500	42
Water	47,350	43
Methyl cyanide	43,800	60
Ethyl cyanide	42,650	48
1:3 dioxalane	48,400	53

Table 3 - Details of the ultraviolet absorption band of halide ion in some solvents which have low dielectric constant.

Solvent	Ion	$\bar{\nu}_{max}$	$10^8 E_{max}$	dE/dT
methylene dichloride	Br^-	45,600	9.1	16±6
	I^-	40,700	15.4	27±7
dioxan	Br^-	44,450 $(\epsilon = 2.(0^5)$	-	30
carbon tetrachloride	Bu_4Br^-	38,650		0

Section (c) - Annex

(1) Research Personnel

	Estimated Number of Hours devoted to Contract	Cost
Professor M.C.R. Symons (Director)	as required	nil
Mr. L. Shields (Research Scholar)	160 hours/month (minimum)	£400 p.a.

(2) Administrative Action - NIL

(3) Cost Breakdown

Charge for expendable supplies and/or materials including chemicals, laboratory glassware, raw materials, compounds, wire, solder, etc.   £250 p.a.

Charge for overhead including such items as heat, light, water, use of laboratory space and facilities, minor administrative services not included under salaries, reproduction of reports, etc.   £60 p.a.

(4) Property acquired at
      contract expense   - NIL